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CATALYST AND PROCESS FOR OXIDATION AND REMOVAL OF NITROGEN OXIDES (NO_x) FROM COMBUSTION GASES

This is a continuation-in-part application of Serial No. 09/225,082, filed January 4, 1999.

Background of Invention

This invention pertains to catalytic oxidation and removal of nitrogen oxides (NO_x) from exhaust gases derived from combustion of hydrocarbon fuels. It pertains particularly to a bi-functional oxidation catalyst and methods for making same for advantageous use in a treatment process for such oxidation of NO_x contained in combustion exhaust gases. The process utilizes an initial catalytic oxidation step and can be followed by further oxidation by a chemical oxidant such as ozone (O₃) for providing essentially complete NO_x oxidation and removal from the combustion gases.

Conventional burning of fossil fuels such as coal, heavy oils and fuel gases to generate heat and energy results in formation of undesired concentrations of nitrogen compounds such as NO_x contained in the resulting combustion exhaust and flue gas streams, and contributes to undesirable air pollution in the atmosphere. At least about 95% of such NO_x in combustion gases is in the form of nitric oxide (NO). Because nitric oxide (NO) is relatively inactive chemically, its removal from combustion flue gas streams by scrubbing with suitable liquids is difficult and inefficient.

Some prior efforts for oxidation of NO_x contained in combustion gases have utilized chemical oxidants such as ozone. For example, U.S. Patent No. 4,011,298 to Fukui et al discloses oxidation and removal of sulfur oxide and nitrogen oxide (NO) from combustion gases by mixing with an ozone-containing gas. U.S. 4,024,219 to Takahashi et al discloses removing nitrogen oxides in waste gases by oxidizing with nitric acid in presence of a porous adsorbent agent such as silica gel or molecular sieves. U.S. 4,035,470 to Senjo et al discloses removal of sulfur oxides and/or nitrogen oxides from waste gases by adding chlorine dioxide or ozone and scrubbing with an aqueous solution. U.S. 4,351,811 to Matsuda et al discloses removing NO and NO₂ contained in exhaust

gases by contact with a metallic oxide catalyst together with ammonia. U.S. 4,564,510 to Bechthold et al discloses removing nitrogen oxides from waste gases by oxidizing with an agent such as ozone to form NO_2 , then adsorbing the NO_2 . U.S. 4,971,777 to Firnhaber et al discloses removing SO_x and NO_x from industrial furnace exhaust gases containing 0.5 vol % O_2 by thermally oxidizing NO at 300-900 C followed by an adsorption step. Also, U.S. 5,206,002 to Skelly et al discloses treating combustion exhaust gases containing oxides of nitrogen and sulfur from an electric power plant by mixing with a chemical oxidant such as ozone (O_3). U.S. 5,756,057 to Tsuchitani et al and U.S. 5,759,947 to Zhou disclose catalysts which can be used for removal of nitrogen oxides from combustion gases. However, it is apparent that known processes for oxidation and removal of nitrogen oxides from combustion exhaust or flue gases have generally been ineffective and undesirable, and that use of ozone alone for NO_x oxidation involves undesirably high operating costs. Thus, further improvements in catalysts and processes for removal of NO_x from combustion exhaust and flue gases are needed in industry for effectively reducing air pollution and smog and providing a clean air environment.

It is known that if the NO_x contained in combustion flue gases could be efficiently oxidized to NO_2 or N_2O_5 , substantial amounts of such oxidized nitrogen compounds could then be effectively removed by liquid scrubbing of the treated flue gases. However, because oxidation of nitrogen oxide NO by O_2 is very slow, improved methods for such oxidation are needed. Combustion flue gases containing NO_x usually also contains some unreacted oxygen, such as 5-10% by volume. It is believed that such oxidation of NO_x could be substantially enhanced by initial adsorption of the NO and the small concentration of O_2 contained in combustion flue gases on a suitable catalytic surface, which also provides simultaneous desorption of an oxidized form of NO_x such as NO_2 from the catalytic surface. Such catalytic oxidation step for NO_x could be followed by further chemical oxidation such as with ozone (O_3) to form N_2O_5 . Because the oxidized NO_x has much greater solubility in suitable scrubbing liquids, substantially all of the NO_x contained in combustion exhaust or flue gases could be effectively removed in the form of oxyacids or salts.

Summary of Invention

This invention provides a bi-functional metal oxide catalyst which is effective for simultaneous

catalytic adsorption and oxidation of nitrogen oxides (NO_x) contained in combustion gases derived from the combustion of hydrocarbon fuels. This bi-functional catalyst composition utilizes specific combinations of active metal oxides which are chemically bonded intimately together so as to form a metal oxide complex having crystalline form or structure which provides both an adsorption function and sites and closely adjacent oxidation function and sites for the NO_x contained in the combustion exhaust or flue gases. Because of its unique composition and structure, this bi-functional catalyst is capable of effectively oxidizing the NO_x to substantially NO_2 at desirable high reaction rates and at relatively low reaction temperatures in the range of 170-550° F. These performance characteristics make this bi-functional catalyst particularly useful for treating NO_x containing flue gases from coal-fired or oil-fired industrial furnaces, or from steam generating boilers in electric power plants to at least partially remove the nitrogen oxides from the combustion flue gases.

Metal oxides which are useful for providing the bi-functional catalyst adsorption function and sites include oxides of metals selected from the group including barium (Ba), cesium (Cs), lanthanum (La), strontium (Sr), zirconium (Zr), and combinations thereof. Metals oxides useful for providing the bi-functional catalyst adjacent oxidation function and sites include oxides of transition metals including chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), manganese (Mn), platinum (Pt) and combinations thereof. The adsorption function metal oxides in the bi-functional catalyst are placed in close intimate contact with the oxidation function metal oxides by utilizing a tri-valent acid binding agent having at least two acid functional groups such as carboxylic acid during preparation of the catalyst. The catalyst also has a balanced molar ratio of the adsorption metals to the oxidation metals within a broad ratio range of 0.1:1 to 5:1, with a molar ratio range of 0.2:1 to 2:1 being preferred. For this bi-functional catalyst, the preferred adsorption metals are barium and lanthanum, and the preferred oxidation metals are copper and manganese with small percentage of platinum as a promotor metal. This invention also includes methods steps utilized for making the bi-functional catalyst, which is initially in powder form but can be deposited on a suitable porous support material or structure.

This invention also provides a process for using the bi-functional catalyst for initial catalytic oxidation of nitrogen oxides NO_x contained in combustion exhaust or flue gases derived from the combustion of hydrocarbonaceous fuels such as coal, heavy oils, and natural gas. In such NO_x initial

oxidation process, the flue gases derived from the fuel combustion and containing up to about 0.5 vol. % NO_x together with 5-10 vol. % O_2 are first contacted by the bi-functional oxidation catalyst of this invention, and for which process the NO_x is adsorbed on the catalytic surface and simultaneously oxidized and desorbed from the catalytic surface at 170-550°F temperature to provide an oxidized form of NO such as at least about 50 vol. % NO_2 , and preferably 60-98 vol. % NO_2 in the treated combustion gas.

In another embodiment of this invention, the partially oxidized NO_x in the combustion exhaust gas downstream from the initial catalytic oxidation step is then preferably further treated by contact with a supplemental chemical oxidant such as hydrogen peroxide (H_2O_2) or ozone (O_3) at reaction temperature of 100-250°F and 0.5-20 psig pressure for providing additional oxidization reactions for converting the NO_2 to higher oxides of nitrogen such as N_2O_5 . For this two-step NO_x oxidation process including the initial catalytic oxidation of NO_x to substantially NO_2 followed by chemical oxidation to substantially N_2O_5 , the initial catalytic oxidation step will preferably utilize the bi-functional catalyst of this invention.

The resulting two-step treated combustion flue gas containing the higher oxidized form of NO_x such as mainly N_2O_5 is next scrubbed by intimate contact with a suitable aqueous scrubbing liquid such as water to remove the oxidized nitrogen compounds from the gas, after which the resulting treated combustion flue gas containing less than about 15 ppm NO_x is discharged to the atmosphere. The scrubbing liquid is further processed as desired to remove the nitrogen compounds such as nitric acid. By utilizing the initial catalytic oxidation step for treating fuel combustion gases, followed by the subsequent chemical oxidation treatment step, significantly less of the chemical oxidant such as hydrogen peroxide (H_2O_2) or ozone (O_3) is required to complete the oxidation of NO_x in the combustion exhaust gases to essentially N_2O_5 . Thus, by utilizing the bi-functional oxidation catalyst in an initial catalytic oxidation step of the two-step NO_x oxidation process according to this invention, the nitrogen oxides (NO_x) contained in combustion gases derived from hydrocarbon fuel combustion are advantageously and effectively transferred from the exhaust or flue gases to a scrubbing liquid, from which the nitrogen oxides can be effectively removed by other known procedures, and the treated combustion gases containing minimal NO_x less than about 15 ppm are discharged to the atmosphere.

This bi-functional oxidation catalyst and two-step process for oxidation and removal of NO_x from combustion gases is useful for fossil fuel fired steam boilers such as used in electric power plants, and for fired industrial furnaces such as used in chemical, glass and petroleum refinery processes.

Description of Invention

The bi-functional oxidation catalyst according to this invention utilizes a unique composition of active metal oxides in which one or more metal oxides selected for providing an adsorption function and sites are provided in close intimate contact with one or more metal oxides selected for effectively providing simultaneous oxidation function and sites on the catalyst. The intimate contact of the adjacent adsorption and oxidation function metal oxides is provided by utilizing a binding acid agent having at least two functional groups such as a carboxylic acid during preparation of the catalyst, so that after a calcining step the metal oxides are chemically bonded intimately together so as to form a metal oxide complex having a crystalline form or structure. The resulting bi-functional catalyst powder material may be coated/supported onto inert geometric shapes or structures having large surface area of at least about $50 \text{ m}^2/\text{g}$ and preferably $100\text{-}500 \text{ m}^2/\text{g}$ which provides low pressure drop for the combustion gases flowing through a catalytic oxidation reactor. The catalyst metal oxides are preferably suitably deposited or embedded onto a stable porous substrate support material such as a ceramic honeycomb structure which is capable of withstanding combustion gas temperatures up to at least about 600°F or higher. Because the bi-functional catalyst of this invention is able to oxidize NO contained in a fuel combustion gas to mainly NO_2 or higher oxides within a desired relatively low temperature range of $170\text{-}550^\circ\text{F}$ and at substantially atmospheric pressure and high space velocity, the catalytic initial oxidation step can be advantageously and conveniently located in commercial electric power plant processes immediately downstream from a particulate solids removal step in the plant boiler section. Accordingly, this bi-functional catalyst and process for utilizing it thereby advantageously avoid any undesired re-heating of the combustion flue gas as would be needed for other oxidation catalysts requiring higher reaction temperatures such as above about 500°F .

The initially oxidized NO_2 contained in the combustion flue gas stream is preferably further oxidized

in a second oxidation step by being mixed with a sufficient amount of a chemical oxidant such as hydrogen peroxide (H_2O_2) or ozone (O_3) to form essentially N_2O_5 at reaction conditions of 100-250°F temperature, 0.5-5psig pressure, and a molar ratio of the chemical oxidant to NO_x of 0.5:1 to 1.2:1. Chemical oxidation conditions of 125-225°F temperature and 0.6-2.0 psig. pressure are usually preferred. Depending upon the percentage catalytic conversion of NO to NO_2 achieved in the initial catalytic oxidation step, the molar ratio of hydrogen peroxide (H_2O_2) to NO_x should be in a range of 0.6:1 to 1.10:1 and the molar ratio of ozone (O_3) to NO_x should be the range of 0.5:1 to about 1.0:1, with lower percentages of catalytic conversion requiring more of the chemical oxidant. Because of the initial catalytic preoxidation step of NO to form substantially NO_2 , only about one-third as much of the chemical oxidant such as ozone (O_3) is required to complete the oxidation of NO_2 to N_2O_5 , as would be required if the chemical oxidant was used alone. Thus, this two-step NO_x oxidation and removal process utilizing the combined catalytic and chemical oxidation steps requires significantly lower process costs for achieving substantially complete removal of NO_x from combustion gases and to meet governmental acceptable levels, such as less than about 15 ppm NO_x , and preferably less than about 10 ppm NO_x remaining in the treated gases discharged to the atmosphere.

Catalyst Preparation Method

The bi-functional catalyst of this invention is prepared by providing the adsorption function metal components including barium, cesium, lanthanum, strontium, zirconium and combinations thereof, and the oxidation function metals components including chromium, cobalt, copper, iron, manganese and combinations thereof, so as to have a molar ratio of the adsorption function metals to the oxidation function metals in the range of 0.1:1 to 5:1, together with about 1 wt. % platinum provided as an oxidation promoter metal. Also for providing the two catalytic metal sites in closely adjacent positions in the bi-functional catalyst, a binding agent such as carboxylic acid having at least two acid functional groups and having a molar ratio of acid to the total metals between 0.5:1 and 2:1, and preferably 0.8:1 and 1.5:1, is utilized for chemically attaching and bonding the adsorptive and oxidative metals intimately together so as to form a metal oxide complex having a crystalline form or structure with the metals arranged in an orderly repetitive pattern between the adsorption metal oxide component and the oxidation metal oxide component.. After an aqueous solution of one or

more of the adsorption metal ions is combined with one or more of the oxidation metal ions within the desired molar ratio range, and the binding acid agent added, the resulting metals compound is dried and calcined in air at 500-800°C (930-1470°F) temperature for 0.4-5 hours to form a fine powder metal oxide precursor material. Such precursor material is then impregnated with another solution of the oxidation function metals sufficient to provide the desired molar ratio of the adsorption metals to the oxidation metals, and the resulting slurry dried and calcined at 500-800°C for 0.5-2.0 hours so as to form a metal oxide complex having a crystalline form or structure in which the metal oxides have an orderly repetitive pattern. Suitable carboxylic acid binding agents and their salts are citric acid and sodium citrate.

A typical bi-functional catalyst of this invention can be prepared utilizing specific procedures as follows:

For preparing the precursor solution including adsorption and oxidation metals, 46.9 grams of BaCuO_2 , 52.3g of $\text{Ba}(\text{NO}_3)_2$ and 46.5g of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{H}_2\text{O}$ are dissolved in 300 ml distilled water, and 76.9g citric acid is dissolved in 200 ml distilled water. The mole ratio between the total metal ions and the citric acid is 1:1. The two solutions are mixed together and water is evaporated at about 95°C (203°F) until a sol consistency is obtained. The sol is further dried at 70°C (158°F) in a vacuum oven, then calcined at about 750°C (1380°F) for 0.5 hours in air, and cooled to provide a Ba/Cu precursor material.

This obtained Ba/Cu precursor material is further impregnated by a Mn and Pt solution, for which 12.1 grams of $\text{Mn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ is dissolved in 100ml distilled water and 1.2 grams 5% Pt solution (ammonia platinum nitrate) is added to the Mn solution. Then 3 grams of the precursor material is impregnated by the Mn and Pt solution to provide the desired molar ratio of the adsorbent metals to the oxidation metals. The resulting slurry is heated during rotation until dried to a solid powder. The solid powder is further heated and calcined at 750°C for 0.5 hours in air, then cooled to room temperature in air to provide a bi-functional catalyst in which the adsorption and oxidation metals are chemically bonded together so as to form a metal oxide complex having a crystalline form.

All other bi-functional catalyst samples were prepared using similar procedures for combining the specific adsorption and oxidation metals closely together so to form a metal oxide complex having a crystalline form, as are listed in Table 1 and 2 of the Examples below.

Brief Description of Drawings

This invention will be described further with reference to the following drawings, in which:

Figure 1 is a schematic flow diagram of a process for catalytic oxidation and removal of NO_x from fuel combustion gases by successive catalytic oxidation and chemical oxidation steps according to the invention;

Figure 2 and 3 are graphs showing catalytic conversion of NO to NO_2 and/or higher oxides utilizing various bi-functional catalyst compositions according to this invention; and

Figure 4 is an x-ray diffraction (XRD) diagram showing the crystalline structure of a typical bi-functional catalyst made according to this invention.

Description of Process

As shown in Figure 1, a hydrocarbon fossil fuel such as particulate coal is provided at 10, and is fed together with combustion air supplied at 11 and preheated at 12 to a burner 13 located in the lower portion of a boiler unit 14. The fuel is combusted with the preheated air in the burner 13 for heating water pressurized to 500-1500 psig and generating pressurized steam. The pressurized water is provided at 16 and preheated at 17, then is further heated and vaporized in heat exchanger 18 to produce the pressurized steam which is removed at 19.

The resulting hot flue gases containing CO_2 , CO and some undesirable nitrogen and sulfur oxides are removed from the boiler unit 14 as stream 20 and passed through an electronic precipitator unit 22, from which fine particulate ash solids are withdrawn at 21. The resulting cleaned combustion gas stream at 23 containing up to about 0.2 vol. % NO_x and 5 – 10 vol.% oxygen is removed by

exhaust fan 24 and is passed as stream 25 at temperatures of 170-550°F and pressure of 0.8-5.0 psig to an initial catalytic oxidation unit 26. The catalytic oxidation unit 26 has a suitable oxidation catalyst material 27 provided on inner surfaces of the oxidation unit. The catalyst 27 is preferably the bi-functional oxidation catalyst as disclosed herein above. However, other known effective oxidative catalyst materials capable of NO_x oxidation at temperatures below about 550°F could be utilized in the catalytic oxidation unit 26. The oxidation catalyst material 27 is coated/supported on a suitable geometric structure providing large surface area such as at least about 50 m²/gm and need not exceed about 500 m²/gm, provides low pressure drop less than about 5 psi and preferably less than 0.5 psi for the flowing gas stream, and is capable of withstanding temperatures up to about 700°F without significant damage.

In the catalytic oxidation unit 26, the treated flue gas stream 25 is partially oxidized by contact with the catalyst material 27, so that the NO_x component contained in the flue gas stream 25 together with 5-10 vol.% oxygen is partially oxidized to form at least about 50 vol. % NO₂ and preferably 60-98 vol. % NO₂ and higher oxides. The oxidation reaction conditions in unit 26 are maintained within the ranges 170-550° F temperature, 0.5-20 psig. static pressure, and at gas space velocity of 5,000-100,000 hr⁻¹. Preferred reaction conditions are 200-400°F temperature, 1-15 psig. pressure, and gas space velocity of 8,000-50,000 hr⁻¹.

The resulting catalytically treated combustion gas stream at 28 containing partially oxidized NO_x is mixed in chemical oxidation reactor 30 with sufficient ozone (O₃) gas provided at 29 such as from an ozone generator to provide further oxidation of the NO₂ to essentially N₂O₅. In the oxidation reactor 30, a molar ratio of O₃ to NO_x is at least about 0.5:1 and need not exceed about 1:1. The gas residence time in reactor 30 is dependent on the initial concentration of the NO_x and sulfur oxides and the reaction temperature, and need not exceed about 10 seconds at about 100-250°F. temperature. The NO_x concentration in the chemically oxidized combustion flue gas at 31 is reduced to a desired low level as required by governmental emission control standards, such as less than about 15 ppm NO_x and preferably less than 10 ppm NO_x.

From the chemical oxidation reactor 30, the resulting combustion gas at 31 containing essentially fully oxidized N₂O₅ is next scrubbed in a scrubber unit 32 against a suitable scrubbing liquid

provided at 33, such as water or a lime solution. The scrubbing liquid is circulated from the scrubber unit 32 lower portion 32a of the by recycle pump 34 through a suitable liquid distributor means 35 including multiple spray nozzles provided in the scrubber 32 upper portion. Make-up scrubbing liquid is provided at 33 to the scrubber unit 32 as needed. After scrubbing, the resulting cleaned flue gas stream containing essentially no NO_x is discharged at 36 to the atmosphere. A portion of the scrubber liquid containing the dissolved nitrogen oxides is withdrawn at 38 from the scrubber 32 and passed to a liquid-solids separation step at 40, from which liquids are removed at 41 and solids are withdrawn at 42 for further use or for suitable disposal.

The bi-functional catalyst of this invention will be described further by use of the following examples, which should not be construed as being limiting in scope.

Example 1

Several bi-functional catalyst powder samples were prepared which each utilized barium, lanthanum, strontium, or zirconium as the adsorption metal ions and oxidation metals ions of copper, manganese and platinum in a molar ratio of the adsorption metal to the oxidation metals within a range 1:3 to 1:6 (0.33:1 to 0.16:1), with the platinum as a promotor metal. A precursor solution was prepared including adsorption and oxidation oxides, for which 46.9 grams of BaCuO_2 , 52.3g of $\text{Ba}(\text{NO}_3)_2$ and 46.5g of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{H}_2\text{O}$ are dissolved in 300 ml distilled water. Also, 76.9g citric acid was dissolved in 200 ml distilled water. The mole ratio between the citric acid and total metal ions was 1:1. The two solutions were mixed together and water was evaporated using a rotary evaporator at 95°C (203°F) until a sol consistency was obtained. The sol was further dried at 750°C (158°F) in a vacuum oven, then it was calcined at about 750°C (1380°F) for 0.5 hours in air, and then cooled to provide the precursor Ba/Cu material.

This obtained Ba/Cu precursor material was further impregnated by a Mn and Pt solution, for which 12.1 grams of $\text{Mn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ was dissolved in 100ml distilled water, and 1.2 grams 5% Pt solution (ammonia platinum nitrate) was added to the Mn solution. Then 3 grams of the Ba/Cu precursor material was impregnated by the Mn and Pt solution to provide the desired molar ratio of the adsorbent metals to the oxidation metals. The resulting slurry was heated with an infrared lamp

during rotation until it was dried to a solid powder. The obtained solid powder was heated and calcined at 750 °C (1380 °F) for 0.5 hours in air, then cooled to room temperature in air to provide the bi-functional catalyst sample.

Example 2

Another sample of the bi-functional catalyst was prepared, for which 43.30 g $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and 18.61 g $\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{H}_2\text{O}$ was dissolved in 150 mL distilled water. Also, 34.58 g citric acid was dissolved in 200 ml distilled water. The mole ratio between the citric acid and total metal ions was 1:1. The two solutions were mixed together, and water was evaporated using a rotary evaporator at 95°C until a sol consistency was obtained. The sol was further dried at 100°C in a vacuum oven to provide a solid amorphous La/Cu precursor. This precursor was heated to 750°C at 10°C/minute rate and calcined at 750 °C for 0.5 hours in air, then cooled to room temperature in air. The precursor formed is 22 grams $\text{La Cu}_{0.8}\text{O}_{2.3}$.

This precursor was impregnated with a Mn and Pt solution, for which 22.25 grams of $\text{Mn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ was dissolved in 100 ml distilled water. The 2.1 grams 5% Pt solution (ammonia platinum nitrate) was added to the Mn solution. 5 grams of the $\text{La Cu}_{0.8}\text{O}_{2.3}$ precursor was impregnated by this solution, the resulting slurry was dried by heating with an infrared lamp during rotation, and further dried in an oven at 100 °C overnight. The solid sample was heated from 25 °C to 750 °C at 10 °C/minute rate and calcined at 750 °C for 0.5 hours in air, and then cooled down to room temperature in air. This sample was examined by x-ray diffraction (XRD) and the results provided in Figure 4 clearly showed that the catalyst sample had a crystalline structure. This sample was used as catalyst D-2 for Example 3.

Example 3

For determining the NO conversion effectiveness of each catalyst sample, a 10 ml size tubular reactor was packed with 5.4 ml of each catalyst sample and a feed gas containing 525 ppm NO and 7.0 vol. % oxygen in nitrogen was passed through the reactor at 900 ml/minute flow rate and at a

pressure range of 0-20 psig. The catalyst sample compositions and their molar ratios of adsorption metal to oxidation metals, reaction temperatures, and the resulting volume percentage NO conversion to NO₂ or higher oxides are listed below in Table1:

TABLE 1
CATALYTIC OXIDATION OF NO TO NO₂

<u>Catalyst Designation</u>	<u>Catalyst Composition and Molar Ratios</u>	<u>Reactor Temperature, ° F</u>	<u>NO Conversion to NO₂, Vol %</u>
A.	49.5%BaCuO ₂ /49.5%MnO/1%PtO ₂ Ba: (Cu+Mn) = 1:4.3	510	92
		488	89
		465	74
		419	66
		377	57
		341	47
		287	41
B.	49.5%BaCuO ₂ /49.5%CuO/1%PtO ₂ Ba:Cu = 1:3.9	423	99
		398	92
		388	88
		352	51
C.	49.5%SrCuO ₂ /49.5%MnO/1%Pt O ₂ Sr: (Cu+Mn) = 1:3.7	522	87
		462	71
		387	51
		318	19
D.	49.5%LaCuO _{2.5} /49.5MnO/1%Pt O ₂ La: (Cu+Mn) = 1:4.4	525	92
		505	93
		477	95
		455	95
		425	94
		374	86
		324	77
		273	72
E.	49.5%ZrCuO ₃ /49.5%MnO/1%Pt O ₂ Zr: (Cu+Mn) = 1:3.9	222	67
		172	62
		508	77
		466	63
		406	45
		363	31
		314	21

These NO conversion to NO₂ results are also shown in graphical form in Fig. 2.

From the results provided in Table 1 and Fig. 2, it is seen that for these bi-functional catalyst samples designated A-E having the adsorption and oxidation metal oxides each provided in intimate contact and balanced molar ratio within the desired molar ratio range of about 1:3.7 to 1:4.4 and at reaction temperatures of 170-525°F, the volume percent of NO conversion to NO₂ and higher oxides of nitrogen generally increases directly with increased reaction temperature up to about 500°F and then may decline slightly. Also, nitric oxide (NO) conversions to NO₂ above about 50 vol. % are achieved at catalytic reaction temperatures within the range of 170-525°F depending upon the particular catalyst composition. The most effective bi-functional catalyst was catalyst sample D which utilized La, Cu and Mn in molar ratio La: (Cu + Mn) of about 1:4.4, and achieved conversions of NO to NO₂ of 95 vol. % at 425-480°F. temperature.

Example 4

Because the NO conversion to NO₂ results for the bi-functional catalyst sample D utilizing 49.5% La CuO_{2.5}/49.5% MnO/1% PtO₂ were generally better than for the other catalyst compositions, additional samples were prepared and examined for which the relative amounts of La, Cu, and Mn were varied. Several additional experimental runs were made at the same reaction conditions as for Example 3. The molar ratios of La to Cu+Mn, the reaction temperatures, and the conversion results of NO oxidation to NO₂ are shown in Table 2 below, and are shown in graphical form by Fig. 3.

TABLE 2
CATALYTIC OXIDATION OF NO TO NO₂

Catalyst Designation	Catalyst Composition And Molar Ratios	Reactor Temperature, ° F	NO Conversion to NO₂, Vol %
D-1	49.5% LaCu _{0.6} O _{2.1} /49.5%MnO/1%PtO ₂ La: (Cu+Mn) = 1:3.5	519	93
		469	95
		419	95
		369	91
		319	83
		270	76
		220	68
		170	58
D-2	49.5% LaCu _{0.8} O _{2.3} /49.5%MnO/1%PtO ₂ La: (Cu+Mn) = 1:4.0	527	91
		477	95
		427	96
		376	93
		326	88
		275	83
		224	77
		173	68
D-3	49.5% LaCu _{1.2} O _{2.7} /49.5%MnO/1%PtO ₂ La: (Cu+Mn) = 1:4.8	519	94
		469	95
		419	93
		370	87
		320	80
		270	73
		220	66
		170	58
D-4	47 LaCu _{0.8} O _{2.3} /52%MnO/1%PtO ₂ La: (Cu+Mn) = 1:4.3	525	91
		475	95
		426	94
		375	87
		325	79
		274	71
		223	64
D-5	55 LaCu _{0.8} O _{2.3} /44%MnO/1%PtO ₂ La: (Cu+Mn) = 1:4.3	519	92
		469	94
		419	91
		369	84
		319	75
		269	68
		220	62

TABLE 2 (continued)

CATALYTIC OXIDATION OF NO TO NO₂

<u>Catalyst Designation</u>	<u>Catalyst Composition and Molar Ratios</u>	<u>Reactor Temperature, °F</u>	<u>NO Conversion to NO₂, Vol %</u>
D-6	43% LaCuO _{2.5} /56%MnO/1%Pt O ₂ La: (Cu+Mn) = 1:5.4	519	92
		469	95
		419	93
		369	85
		319	75
D-7	52% LaCuO _{2.5} /47%MnO/1%Pt O ₂ La: (Cu+Mn) = 1:4.1	527	93
		474	96
		424	95
		374	90
		323	84
		273	78
		223	72
		172	62

From the above results provided in Table 2 and Fig. 3, it is seen that the percentage NO conversion to NO₂ increased rather directly with increased temperature up to about 90-95 vol. % at 350-500°F. and then declined slightly. The most effective bi-functional catalyst combination of La CuO and MnO was sample D-2 having composition of 49.5% La Cu_{0.8} O_{2.3}/49.5% MnO/1% Pt O₂ and a molar ratio of La: (Cu + Mn) in the range of 1:4.0.

Although the bi-functional oxidation catalyst material and process for utilizing the catalyst of this invention for NO_x oxidation and removal have been described broadly and also in terms of preferred catalyst composition and also catalytic oxidation process steps and reaction conditions, it is understood that modifications and variations can be made all within the scope of the invention as defined by the following claims.